

(In press)
nature

NSG-257
b
NCR-44-005-020

FACILITY FORM 602	N67 18140	(ACCESSION NUMBER)		(THRU)
	34	(PAGES)		(CODE)
	CR-81776	(NASA CR OR TMX OR AD NUMBER)		(CATEGORY)

ALIPHATIC HYDROCARBONS

IN PRECAMBRIAN ROCKS

By Professor J. Oro' and D. W. Nooner

Department of Chemistry

University of Houston

Houston, Texas 77004

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) 3.00

Microfiche (MF) 1.65

High molecular weight alkanes including the saturated isoprenoid hydrocarbons, pristane and phytane, have been found in shale 1 billion years old from the Nonesuch formation^{1,2}, chert 2 billion years old from the Gunflint iron formation of Ontario, Canada³, and rocks (carbonaceous lens and graphitic-like silicates) 2.7 billion years old from the Soudan iron formation of Minnesota⁴⁻⁶. The biogenic origin of the organic materials in the Nonesuch shale and the Gunflint chert has been assigned on the basis of fossil microorganisms contained in them⁷ and the hydrocarbons were considered to be remnants of this early life.

We have analyzed 3.2 billion year old sedimentary rocks from the Fig Tree series of the Swaziland system, eastern Transvaal, South Africa, for aliphatic hydrocarbons, utilizing techniques described in detail elsewhere^{6,8,9}. The carbonaceous silicate rocks from the Fig Tree series were collected by Dr. T. C. Hoering the Sheba gold mine near Barberton, South Africa, and by Dr. E. S. Barghoorn in an outcrop near the Daylight mine, 28 km. east-northeast of Barberton. The rocks were black chert (sample no. 1) and a carbonaceous graphitic-like silicate (sample no. 2) collected by Hoering, and black chert (sample no. 3) collected by Barghoorn. In addition, an extract obtained by Hoering from a core specimen of shale (sample no. 4) was analyzed.

The procedure used with samples 1, 2 and 3 was to pulverize the rocks (after appropriate steps had been taken to remove

surface contamination) in a Carver press test cylinder, and extract the organic compounds with benzene-methanol (3:1) in an all-glass Soxhlet-type extractor. The extract supplied by Hoering was obtained from sample no. 4 by extracting three to four hundred grams of the crushed shale (core sample) in an ultrasonic generator with n-pentane. The solvent extracts were then fractionated on silica gel. The procedure of Meinschein and Kenny⁹ was followed except that the aliphatic hydrocarbons were eluted with n-pentane in the case of sample no. 4. By carefully blowing the low boiling solvent (n-pentane) to a very small volume, many of the relatively low molecular weight hydrocarbons, ordinarily lost by evaporation to dryness when n-heptane is used, were recovered.

The eluates were dissolved in benzene and suitable aliquots taken for analysis by gas chromatography and combined gas chromatography-mass spectrometry.¹⁰ For the gas chromatographic analyses tentative identification of the separated compounds was obtained by (1) coinjection of pristane, phytane, n-octadecane, and n-octadecene-1 with the samples (samples 1 and 4) on capillaries coated with Polysev (m-bis-m-(phenoxyphenoxy)-phenoxybenzene). and (2) comparison of the retention times of the compounds in the samples (samples 1-4) with those of appropriate hydrocarbon standards (normal alkanes, pristane, phytane, n-hexadecene-1, n-octadecene-1, n-eicosene-1, and n-tricosene-1) chromatographed on the same columns (Polysev) and at the same conditions. For the graphitic-like silicate (sample no. 2), in addition to the com-

parison of retention times of eluted components and standards (normal hydrocarbons, pristane, and phytane) made with Polysev as the liquid phase, similar comparisons were made using a 15 m packed column with SE-30 as the liquid phase.

Mass spectrometric identifications (samples 1 and 4) were made by taking individual mass spectra of the individual components as they were eluted from the Polysev coated capillary¹¹. These spectra were compared with spectra of the aforementioned standards obtained in the same manner. Since we did not have a standard, the assignment of norpristane was made by comparing our mass spectrum with available C_{18} isoprenoid mass spectra.²

Figure 1 shows the chromatograms obtained using Polysev as the liquid phase in stainless steel capillary columns. The hydrocarbons shown in Figure 1A were obtained from the internal part of a chert sample (sample no. 1), which was treated with chromic acid cleaning solution prior to crushing and extracting. Normal alkanes ranging from C_{15} through C_{26} were found to be present. The peaks designated as a and b correspond by their chromatographic position to pristane and phytane, respectively. The peak immediately following $n-C_{16}$ contains $\Delta-C_{16}$, but probably also contains norpristane. The shape of the peak clearly shows that it represents at least two compounds. The peaks immediately following $n-C_{18}$, $n-C_{20}$, and $n-C_{22}$ correspond to the

normal C_{18} , C_{20} and C_{22} monoenes respectively. The retention times do not correspond to the respective n-alkylcyclohexanes. The retention times of these cyclic alkanes (on Polysev) almost coincide with those of normal alkanes having one more carbon. As indicated earlier, the identification of the olefins was made on the basis of both mass spectrom^{etric} analysis and retention times of known hydrocarbons (normal C_{16} , C_{18} , C_{20} , and C_{22} monoenes). The gas chromatographic analysis of this sample made on the LKB 9000 instrument is shown in Figure 1E.

A second analytical determination of alkanes was carried out with small pieces (inside and outside) of the same specimen of chert. The decontamination of possible surface contaminants was performed this time not by treatment with chromic acid, but by carefully extracting the rock surface with organic solvent (benzene methanol, 3:1). After extraction the pieces were then dried, crushed, extracted and the extract analyzed.

The chromatographic pattern of the paraffinic hydrocarbons recovered from the sample is shown in Figure 1C. As shown, the chromatographic pattern is the same as that of Figure 1A. Approximately the same level of hydrocarbons (0.02 ppm) was found in sample no. 1 by the two separate and slightly different analytical determinations. The mass spectrometric results of the second determination were essentially as obtained for the first. Furthermore, in the second analysis, two mass spectra were taken of the peak

immediately following $n\text{-C}_{16}$, one on the ascending side of the peak before inflection and the other on the descending side. The components of this peak were found in fact to be norpristane and C_{16} monoene as indicated by the first analysis. The mass spectra of the isoprenoid hydrocarbons of this sample are presented in Figure 2. They are essentially identical to those given by standards. The controls or procedural blanks (glass was carried through all analytical steps including pulverization in the Carver press associated with the particular samples) are shown in Figures 1B and 1D. As seen the alkane contribution of the blanks amounts to less than 1% and 5% respectively of the amounts found in the actual samples.

Sample no. 2 (graphitic-like silicate obtained from Hoering) and sample no. 3 (black chert obtained from Barghoorn) were boiled in benzene-methanol (3:1) to remove any possible surface contamination. The n -heptane eluates from these samples were analyzed on a 305 m long x 0.76 mm inside diameter stainless steel capillary coated with Poly-sev. Extremely low levels of hydrocarbons (approximately 0.003 ppm) were obtained. Small peaks representing hydrocarbons in the $\text{C}_{12}\text{-C}_{19}$ range were obtained. Peaks having the retention time of pristane and phytane standards were detected in the graphitic-like silicate, but not in the chert. The much lower yields obtained with these two samples show that significant variations in the hydrocarbon

content of these rocks exist. In general, variations in hydrocarbon content can be expected from different samples of the same sediment. Indeed, significant variations have been observed in our laboratory in rocks from the Gunflint iron formation of southern Ontario. The existence of such hydrocarbon-deficient rocks makes it possible to run ideal analytical controls for samples from the same formation which may be richer in hydrocarbons. The heterogeneity of quantitative distribution of hydrocarbons may be the result of differences in the concentration or composition of organic matter or in the thermal metamorphism of the rocks analyzed. This heterogeneity may be taken as an indication that the hydrocarbons were not incorporated into the rocks by a general process of petroleum migration in more recent times.

In order to obtain additional data on Fig Tree Precambrian sediments, a core of the Fig Tree shale (sample no. 4) was extracted (see above) more recently at the Geophysical Laboratory of the Carnegie Institute of Washington by Dr. T. C. Hoering, and the resulting hydrocarbons were analyzed at Houston. The results obtained were similar to those of Figure 1 except that more of the low molecular weight alkanes and less of the higher molecular weight paraffins were detected. This is indeed what would be expected by the use of n-pentane as a solvent instead of n-heptane. The amounts of hydrocarbons were of the order of 0.15 ppm.

Aliphatic hydrocarbons are present in the Fig Tree rocks at extremely low levels (0.003-0.15 ppm). Sufficient data are not available to ascertain whether or not the hydrocarbons date from deposition. However, the treatment of the samples precludes the hydrocarbons being merely surface contaminants. This conclusion is in line with the fact that the $^{13}\text{C}/^{12}\text{C}$ ratios of the extractable and insoluble organic matter of the Fig Tree rocks are essentially identical¹². However, Hoering's comments¹² on the discrepancies to this correlation that occur for several Precambrian samples indicate that more work on carbon isotope distribution needs to be done before the actual significance of $^{13}\text{C}/^{12}\text{C}$ ratios can be ascertained. Entities have been found in the Fig Tree shale that have the morphology of fossil bacteria and possibly algae¹³ and these hydrocarbons may be remains from this early life.

The occurrence of olefins in some samples of Fig Tree chert is somewhat unexpected. Although olefins have been observed in Pennsylvania crude¹⁴, in general they are relatively rare in petroleum crudes and sediments. Their presence in the cherty Precambrian sediment is not easily understood unless one assumes that the olefins can be preserved in the chert matrix, for long periods of time or that they may be products of the thermal degradation of biological compounds such as even carbon-numbered alcohols.

The relative large amounts of pristane found in the sediment may be taken as an indication that the isoprenoid

hydrocarbons are probably biogenic. However, it has been demonstrated that 2-methylbutane (isoprane) and other branched hydrocarbons can be synthesized by Fischer-Tropsch processes^{15,16}. Thus, it is not impossible that certain isoprenoid hydrocarbons could also be formed abiotically. Yet, more work needs to be done on this type of synthesis before advancing any speculations.

To our knowledge no assignment of configuration to the asymmetric centers of fossil pristane and phytane has been made. With the further development of some recent techniques using optically active phases¹⁷ it may eventually be possible to separate the stereoisomers (e.g. enantiomers, diastereomers) of pristane and phytane. Then the aforementioned assignments of configuration would be feasible and it might be possible to differentiate between abiologically and biologically derived isoprenoids. Although we do not know the isomeric forms of the isoprenoid structures examined, we do not believe, on the basis of the gas chromatographic and mass spectrometric data, the compounds to be isomers in which methyl substituents are displaced from the positions found in pristane and phytane. Nevertheless, it is possible that our methods might not detect a shift in position of only one methyl group.

After completing this work, we have learned that isoprenoid and paraffinic hydrocarbons have also been detected by other workers in samples of the Fig Tree chert which had apparently undergone a minimum amount of thermal metamorphism¹⁸ and in similar rocks which presumably were more

metamorphosed¹². The organic geochemistry of Precambrian sediments and the problems involved in assessing the role of contamination and metamorphism, and determining whether the hydrocarbons date from sediment desposition or are the result of later infiltrations into the rock have been recently discussed in some detail by Hoering¹².

Because of the compact nature of some of these rocks, especially the chert, and the fact that internal samples were analyzed in most cases, it is probable that the hydrocarbons are indigenous to the rock. The fact that microfossils have been found in some of these rocks would suggest a biochemical origin for these hydrocarbons which took place about 3.2×10^9 years ago. However, additional research work will have to be carried out in order to decide in a more definite way whether these hydrocarbons date from sediment deposition and whether they are biogenic or not.

ACKNOWLEDGMENT

We thank T. C. Hoering, E. S. Barghoorn and W. G. Meinschein for samples and valuable comments. This work was presented at the 4th meeting of the Group for the Analysis of Carbon Compounds in Carbonaceous Chondrites, Washington, April 21, 1966 and at the 3rd International Meeting on Organic Geochemistry, London, September 28, 1966. It was supported in part by NASA Research Grants (NsG-257 and NGR-44-005-020) from the National Aeronautics and Space Administration.

1. Meinschein, W. G., Barghoorn, E. S., and Schopf, J. W.
Science, 145, 262 (1964); Barghoorn, E. S., Meinschein,
W. G., and Schopf, J. W., Science, 148, 461 (1965).
2. Eglinton, G., Scott, P. M., Belsky, T., Burlingame, A. L.,
and Calvin, M., Science, 145, 263 (1965); Eglinton, G.,
Scott, P. M., Belsky, T., Burlingame, A. L., Richter, W.,
and Calvin, M., Space Science Laboratory, University of
California, Technical Report Series No. 6, Issue No. 9,
January 1965.
3. Oro', J., Nooner, D. W., Zlatkis, A., Wikstrom, S. A.,
Barghoorn, E. S., Science, 148, 77 (1965).
4. Belsky, T., John, R. B., McCarthy E. D., Burlingame, A. L.,
Richter, N., and Calvin, M., Nature, 206, 446 (1965).
Meinschein, W. G., Science, 150, 601 (1965).
5. Meinschein, W. H. Science, 150, 601 (1965).
6. Oro', J., Nooner, D. W., Zlatkis, A., and Wikström, S. A.,
Life Sc. Space Res., 4, 63 (1966).
7. Tyler, S. A., and Barghoorn, E. S., Science, 119, 606 (1964)
Barghoorn, E. S., and Tyler, S. A., Ann. N. Y. Acad. Sci.,
108, 451 (1963), Science, 147, 563 (1965).
8. Oro', J., Nooner, D. W., and Wikstrom, S. A., Science, 147,
870 (1965).
9. Meinschein, W. G., and Kenny G. S. Anal. Chem, 29, 1153
(1957).
10. Ryhage, R., Anal. Chem., 36, 759 (1964); Watson, J. T., and
Biemann, K., Anal. Chem., 36, 1135 (1964); Ryhage, R.,
Wikström, S., and Waller, G. R., Anal. Chem., 37, 435 (1965).

11. Oro', J., Han, J., and Zlatkis, A., Anal. Chem., 39, 27 (1967); Oro', J., and Han, J., J. Gas Chromatog., 5 (1967) (in the press); Nooner, D. W., and Oro', J., Geochim. Cosmochim. Acta. (to be published, 1967).
12. Hoering, T. C., in Researches in Geochemistry, Vol. II, edit. P. H. Abelson (John Wiley, N. Y., in press).
13. Barghoorn, E. S., and Schopf, J. S., Science 152, 758 (1966).
14. Fred, M., and Putscher, R., Anal. Chem., 21, 900 (1949); Haak, F. A., and Van Nes, K., J. Inst. Petrol., 37, 245 (1951).
15. Sharkey, A. G., Jr., Shultz, J. L., and Friedel, R. A., Anal. Chem., 34, 826 (1962); Friedel, R. A., and Sharkey, A. G., Jr., Science, 139, 1203 (1963).
16. Oro', J., in "The Origin of Prebiological Systems and of Their Molecular Matrices", Fox, S. W., ed. Academic Press, New York and London, 1965, pp. 137-162.
17. Feibush, B., and Gil-Av, E., J. Gas Chromatog. in press.
18. Meinschein, W. G., (Personal communication). See also reference 13.

Figure 1. Gas chromatographic separation of alkanes from the Fig Tree chert with capillary columns (Polysev).

- (A) Stainless steel tubing 91.5 m x 0.076 mm, coated with Polysev. F and M model 810 gas chromatograph equipped with a flame ionization detector. Nitrogen pressure, 1050 g/cm². No split. Chert extracted (pulverized inside piece), 100.5 grams. About $\frac{1}{2}$ of the n-heptane eluate was injected. Range 10; attenuation, 4. Isothermal at 140° C for 22 minutes, then programmed at approximately 6° C per minute to 200° C.
- (B) Blank (pulverized glass substituted for sample), treated in the same way as the sample.
- (C) Analytical equipment and conditions same as in (A). Chert extracted (pulverized piece which included some solvent-cleaned outside material), 97.9 grams. About $\frac{1}{2}$ of the n-heptane eluate was injected.
- (D) Blank (pulverized glass substituted for sample), treated as sample.
- (E) Stainless steel tubing, 75 m x 0.76 mm, coated with Polysev. LKB 9000 gas chromatograph-mass spectrometer combination. Helium flow, 24 ml/min. No split. Same sample and eluate as in A. About 1/3 of the eluate was injected. Gain, 6. Isothermal at 130° C

for 18 minutes, then programmed at approximately
1.5°C per minute to 200°C.

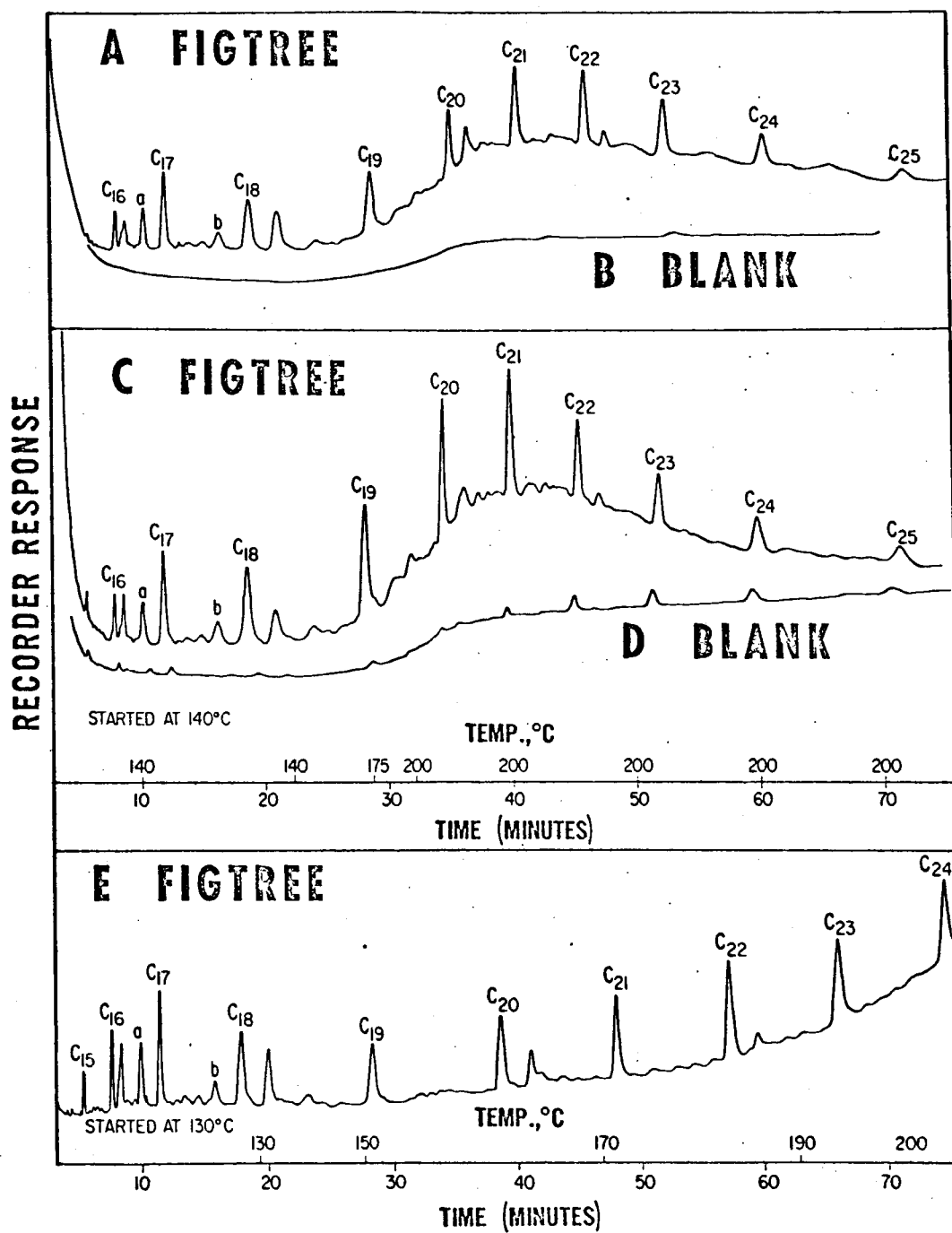


Figure 2

Mass spectra of saturated isoprenoid hydrocarbons from the Fig Tree chert sample extracted in Houston. Obtained using an LKB 9000 gas chromatograph-mass spectrometer combination.

